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R_2Fe_{17} and RM_{12} carbide and carbonitride synthesis from heavy hydrocarbon compounds*

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Abstract

A new route for the synthesis of carbides and carbonitrides of R_2Fe_{17} compounds is presented. Using heavy hydrocarbon organic compounds, it is possible to obtain carbides and carbonitrides without the formation of α-iron. *In situ* powder neutron diffraction experiments, thermomagnetic analysis and scanning electron microscopy and energy-dispersive X-ray techniques have been used to determine the best reaction conditions and to analyse the products of the reaction. The method has also been applied to compounds of the RM_{12} series.

1. Introduction

The recently discovered [1, 2] ternary carbides and nitrides of formulae $R_2Fe_{17}X_{x\leqslant 3}$ and $RM_{12}X_{x\leqslant 1}$ (R, rare earth metal; $X\equiv C$, N; $M\equiv Fe_{1-y}M_y'$) exhibit strongly improved magnetic characteristics in comparison with the starting binary alloys. Interstitial insertion yields a doubling of the Curie temperature and increased magnetocrystalline anisotropy, making the new series very promising for hard magnet utilization.

First only non-stoichiometric carbides were synthesized using a high temperature solid–solid reaction [1]. Then the nitrides were obtained by reacting gases (NH_3, N_2) at rather low temperatures on finely divided powders [2]. Moderated synthesis conditions improve the saturation of the ternaries and avoid a disproportionation process dramatically activated by temperature and time. Such a technique was discovered to apply also to carbide formation using hydrocarbon gases (*e.g.* butane, methane, acetylene) which are decomposed on the powdered samples [3]. These conditions were also applied to the synthesis of other ternaries with the $ThMn_{12}$ type of structure [4].

In order to control the insertion process better, we have developed here appropriate synthesis techniques. In a series of papers [5–8] we have reported precise crystal and magnetic features and discussed the limits of the non-metal stoichiometry in comparison with previously analysed parent ternary hydrides [9]. The details of the magnetic structure have been interpreted in terms of Fe–Fe exchange interaction enhancement [9] and of the R crystal electric field (CEF) term reinforcement [10] as for the $R_2Fe_{14}BH_x$ series [11].

The insertion activity depends on several parameters but is mainly dominated by the surface barrier reaction, which can be roughly divided into molecule-to-atom adsorption and surface-to-bulk atom diffusion. The reaction kinetics depend on the specific surface area, which can easily be increased by hydrogen decrepitation of the alloys prior to or during the C (or N) insertion process.

Recently we have noticed that the use of a high N_2 pressure yields multiple beneficial effects, making the reaction faster at lower temperature and yielding a final N charge closer to stoichiometry [12]. Such higher quality products can also be formed by the use of hydrocarbons at normal pressure.

The stoichiometry of the final products was checked by neutron diffraction techniques, since neither X-ray diffraction (not able to detect light elements) nor gravimetric analysis of the sample (insensitive to possible disproportionation) appears to be suitable here.

A low temperature reaction favours the formation of rather stable ternary hydrides. A high temperature (*i.e.* 400 °C or more) makes these hydrides unstable

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*Dedicated to Professor E.F. Bertaut in honour of his 80th birthday.

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but, conversely, promotes the formation of ternary carbides. Therefore we have searched for organic materials allowing the immediate transfer of carbon only when the temperature reaches a given value. Thus we propose to use higher stability hydrocarbon materials (and hydrocarbonitrogen) of heavier formula weight, with both a higher thermal stability and a lower H/C(N) ratio than the previously used hydrocarbon gases.

Liquid and solid materials make handling easier, so a large number of such compounds have been tested for their reaction with alloy powders. Some typical examples are reported below.

2. Experimental techniques

Most of the $R_2Fe_{17\pm y}$ alloys ($R \equiv Ce$, Nd, Sm, Ho, Er, etc.) have been studied, of Th_2Ni_{17} as well as Th_2Zn_{17} types, without any significant difference. The techniques we used to prepare the alloys have already been described in detail elsewhere [5]. The annealing procedures were particularly controlled in order to eliminate the residual amount of non-reacted α-iron. Three different types of experiments giving information on the reaction process have been carried out. In all cases the alloy ingots were crushed, ball milled and sieved to a mean particle size of about 25 μm.

The first experiment was done with a vaporized liquid (vapour–solid reaction). It was performed in a reactor with a volume of about 2 l, with pressure and temperature controls, on a few grams (3–5 g) of powder at various temperatures and for various times. Achievement of the reaction was observed from the partial vapour pressure recording. Benzene (C_6H_6) and toluene (C_7H_8) were used as the only carbon suppliers.

In the second type of experiment a thermomagnetic device was used to monitor the reaction and the products formed via their magnetization and Curie temperature. Weighed amounts of alloy powder and solid (or liquid) hydrocarbon (or hydrocarbonitrogen) were sealed into small silica ampoules. In each case 200–300 mg of alloy was used and the heating and cooling cycle was adapted to analyse the reaction kinetics better. This allowed the testing of a large series of organic materials, including rather dense and toxic ones (*e.g.* benzene, toluene, naphthalene, anthracene, pyrrole, triazine, triazole and sulphur-containing compounds such as thiophene or thiazole).

Finally, several time-and-temperature-controlled neutron diffraction experiments were performed using a large aperture (80°, 2Θ) one-dimensional curved detector. The experimental set-up has already been described in ref. 13. Amounts of powder (typically 5g, sieved only to 100 μm) and organic compounds (anthracene, triazole) were sealed in silica tubes and then introduced into a dedicated furnace for neutron diffraction. For the 8 h experiment the temperature of the sample was brought to 420 °C and then maintained at this value during data collection, with a 5 min period of counting time. After the experiment the reacted materials were also checked by X-ray diffraction using the focusing Guinier–Hägg camera technique (λ_{Cr}, K α_1), the photographic films being analysed using a scanner. Selected samples were analysed by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) techniques.

3. Experimental results

3.1. Vapour–solid reactions in a dedicated reactor

An R_2Fe_{17} sample (3–5 g) was placed in a large volume reactor made of silica. The volume was evacuated and rinsed several times with benzene (toluene) vapour. The vapour pressure was maintained close to 0.02 Pa and for several hours a plateau temperature was applied. In less than 3 h the partial pressure was observed to increase and quickly stabilize to two to three times the initial value. This corresponds to the formation of molecular H_2 due to the cracking of the benzenic cycles. Excessive temperatures ($T > 500$ °C) lead to the deposition of large amounts of finely divided carbon particles coating the metal ones, which are almost transformed to α-iron. At low temperatures only parts of the sample were transformed. In the temperature range 480 ± 10 °C a well-crystallized $R_2Fe_{17}C_x$ sample was obtained, shown by X-ray diffraction to be a single phase. The volume derived from measurement of the cell parameters indicates that, based on the results of ref. 14, no less than 2.7 C atoms per formula unit have been inserted. When using toluene instead of benzene, no significant change was observed in the final results.

3.2. Thermomagnetic inverstigations

In order to check liquid and solid hydrocarbon materials with various handling restrictions (hazardous or toxic), weighed amounts of metal powder and organic compounds were sealed in very small evacuated silica ampoules. The dimensions of these sample holders were designed to fit a thermomagnetic Faraday-type apparatus. Initially the starting alloys were examined for their purity, since this technique is very sensitive to magnetic traces (*e.g.* α-Fe). Some typical curves (Fig. 1(a)–1(d)) recorded on heating the mixture allow us to point out the details of the reaction. From these curves it is clear that heating the mixture to too high a temperature leads to a definitive disproportionation. This very fast phenomenon produces large quantities of fine α-iron particles as may be inferred from Fig. 1(d). The heavier the hydrocarbon materials used, the

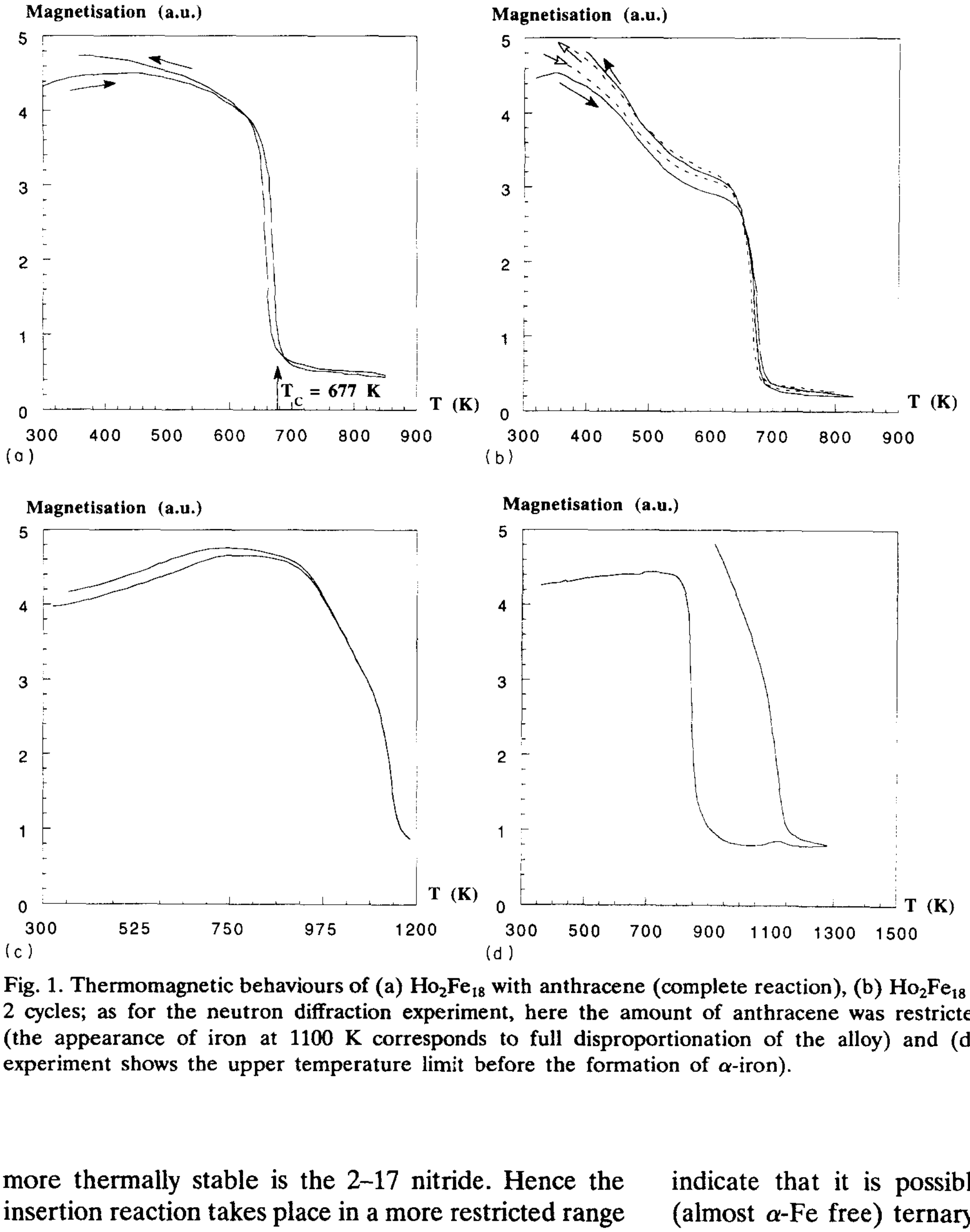


Fig. 1. Thermomagnetic behaviours of (a) Ho_2Fe_{18} with anthracene (complete reaction), (b) Ho_2Fe_{18} with anthracene (partial reaction, 2 cycles; as for the neutron diffraction experiment, here the amount of anthracene was restricted), (c) $YFe_{11}Ti$ with anthracene (the appearance of iron at 1100 K corresponds to full disproportionation of the alloy) and (d) $YFe_{11}Ti$ with anthracene (this experiment shows the upper temperature limit before the formation of α-iron).

more thermally stable is the 2–17 nitride. Hence the insertion reaction takes place in a more restricted range of temperature around the optimal temperature. It is possible to initiate the reaction and saturate R_2Fe_{17} compounds quickly to $R_2Fe_{17}X_x$ with $x \approx 3$, by using the dense hydrocarbon route with the following rules.

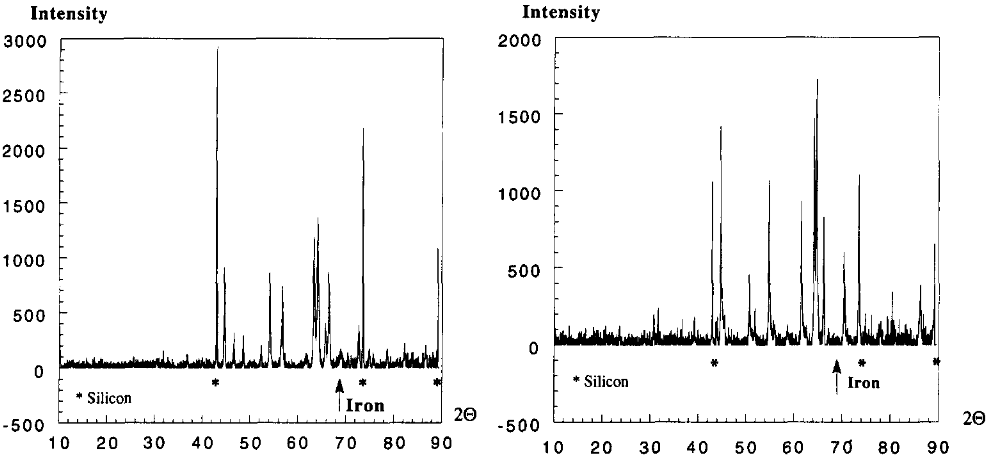
(1) The reaction is initiated at a moderate temperature where the compound can be divided into very small grains, in particular when the stoichiometry $x = 3$ is required.

(2) The reaction is activated by the presence of (limited) amounts of atomic hydrogen, making the alloy surface brittle, larger and cleaner via fresh cracks.

(3) The reaction can be easily controlled by a limited drop in temperature, whereby excess hydrogen can be easily evacuated if it is in too high a concentration.

All the observations obtained using this charging route as well as the route described in Section 3.1 indicate that it is possible to synthesize high purity (almost α-Fe free) ternary carbides and carbonitrides. This is shown in Fig. 2(a) and 2(b), which present the X-ray diffraction patterns recorded for some of these materials using the Guinier–Hägg technique. Carbon and nitrogen can be inserted simultaneously by using *e.g.* triazole ($C_2H_3N_3$) as the interstitial supply material. A very fine modulation of the fundamental properties (T_C, CEF parameters) can be obtained by using appropriate organic mixtures leading to a variable N/C ratio.

Finally, sulphur-containing organic materials were shown to dramatically destroy the starting binary alloys as already observed for direct gas–solid and solid–solid reactions. Both the relatively large size of the sulphur atom and its large electronegativity make it difficult to insert sulphur and to stabilize the hypothetical "$R_2Fe_{17}S_x$" compounds.



(a) (b)

Fig. 2. X-Ray diffraction patterns of (a) $Sm_2Fe_{18}C_x$ and (b) $Ho_2Fe_{18}C_x$ after reaction in the thermomagnetic device.

3.3. *Kinetics of reaction analysed by neutron diffraction*

Figure 3 shows the three-dimensional plot produced by the successive diffraction patterns recorded every 5 min on reacting Ho_2Fe_{18} powder with triazole. After heating from 20 to 420 °C, the sample was reacted until the organic material was completely consumed.

Before refinement of the data a series of facts should be underlined.

(1) The modulations of the background in Fig. 3 arise mainly from the silica glass sample holder. This contribution to the background was observed to be stable and has been interpolated linearly segment by segment for the sequential refinements of the structure.

(2) Only traces of the organic material were observed before their disappearance above 350 °C. Also, we observe the presence of ferromagnetic contributions to the scattering of Ho_2Fe_{18} prior to reaching the Curie temperature ($T_C = 405$ °C).

(3) The reaction is initiated at about 360 °C with the appearance of a ternary compound with distinctly larger cell parameters than the starting alloy.

(4) After the reaction no significant α-Fe is detected from the Bragg lines.

More details are given in a separate paper devoted entirely to this subject [14], but the main aspects of the reactions are described below.

Figure 4(a) shows the cell parameter expansion during the heating phase and then during the constant-temperature activation process upon alloy reaction with anthracene. In the first stage a_A, c_A and a_I (A represents

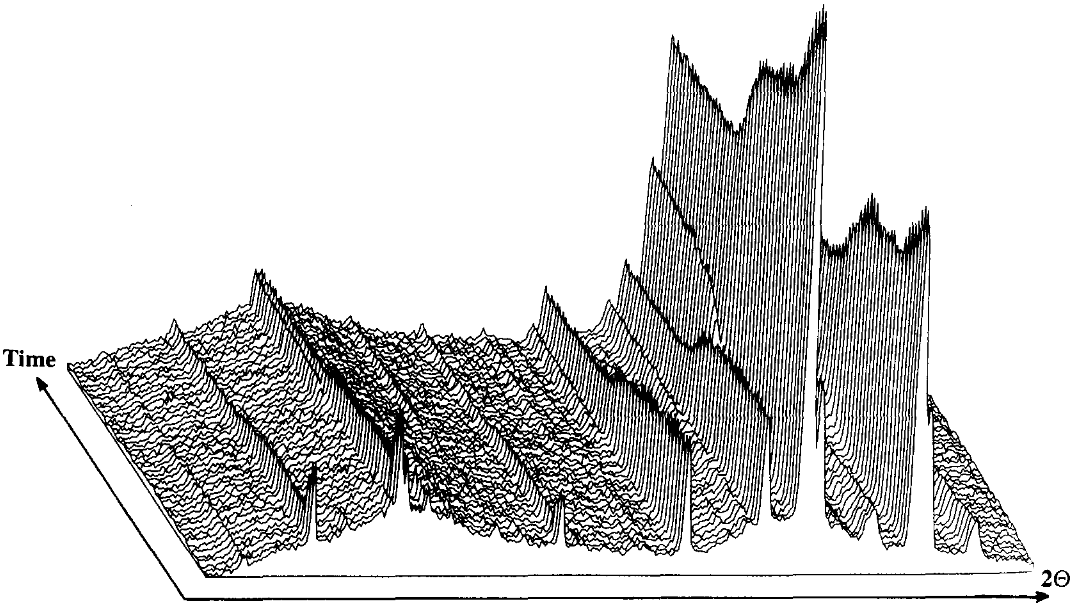


Fig. 3. Neutron thermodiffraction plot of the reaction of Ho_2Fe_{18} with triazole.

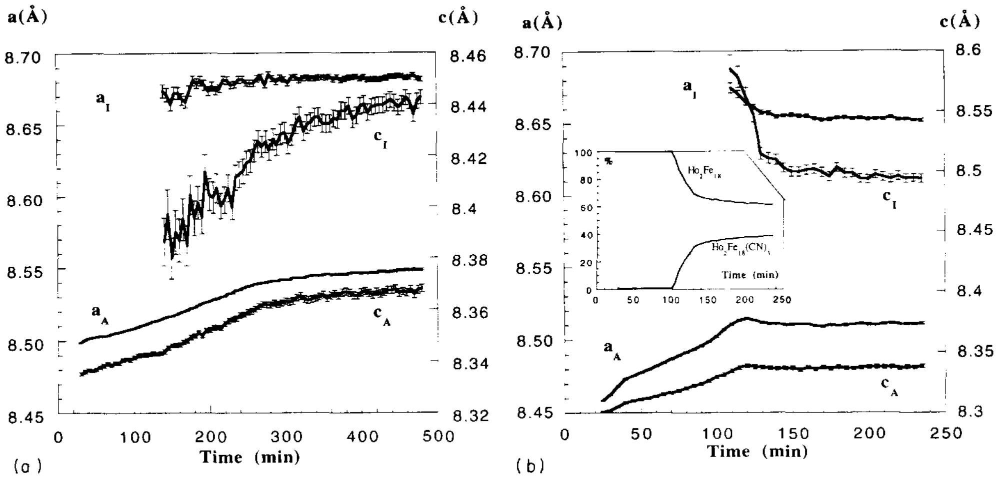


Fig. 4. Cell parameter behaviours of the reactions of Ho_2Fe_{18} with (a) anthracene and (b) triazole. Inset in (b): rate of reaction with triazole.

the unchanged sample, I the interstitial compound) expand almost linearly with time (and temperature up to 364 °C), after which the interstitial insertion starts and accelerates the a_A and c_A behaviour. Simultaneously, c_I increases at a greater rate; it continues to increase but less rapidly when the temperature is maintained constant. Surprisingly, a_A and c_A show a slow rate of expansion during the constant-temperature treatment at 420 °C.

Figure 4(b) shows the cell parameter expansion upon alloy reaction with triazole. As soon as the amount of charged material was sufficient to allow accurate fits to the data, the a_I and c_I cell parameters appeared distinctly reduced from the parent values a_A and c_A, then remained almost constant or decreased slightly. The a_A and c_A parameters expand with temperature and then remain constant during the temperature plateau. This behaviour clearly differs from that of the previous reaction: the reaction rates are markedly different when the alloy is inserted by C or by a mixture of C+N. The diffusion processes should be different for each of the species and pertinent information comes from the behaviour of the octahedral site occupancy number. Using the contrast of the respective neutron-scattering cross-sections of C and N, it appears clear that the absorption process is dominated firstly by the N insertion, then the C/N ratio is progressively re-equilibrated. When parts of the sample are activated further, they participate in an N-to-C exchange making the total occupancy close to three, preventing an intermediate charge from taking place.

3.4. *Microstructure and microanalysis of the alloys charged by $C_{14}H_{10}$ (anthracene) and $C_2H_3N_3$ (triazole)*

By using a Jeol 840A scanning electron microscope on-line equipped with a Quantex EDX analyser, the previous two series of materials were inspected. The lower and upper parts of the powder appeared not to have reacted in the same way, since the organic material introduced into the sealed ampoule was in limited quantity in order to prevent any final excess hydrogen overpressure. Since neutron diffraction analysis has revealed that both unreacted and reacted particles can coexist, the last type was encountered more and more on checking the material from the bottom to the top of the sample (and reciprocally). After the reaction with anthracene the reacted grains examined by SEM show cracks almost equally spaced on the surface and equally distributed in size (2–4 μm) as seen in Fig. 5(a) and 5(b). In these figures it is possible to distinguish different amplitudes in the cracking process, probably depending on the size of the initial grain (25 μm or less) and its location in the ampoule. Few Ho-rich grains have been identified, the microanalysis technique being unable to identify definitively the presence of a light element such as carbon in the particles. However, a low electron energy (5 keV) analysis of the large but changed particles indicates the formation of a ternary carbide with the ratio C/(Ho+Fe) almost constant. In contrast, the flat surfaces of the virgin particles are of a pure binary composition.

Flat-surfaced and unreacted grains were found mainly in the upper part of the sample. Directly in contact with the organic material, the bottom part of the powder appears fully reacted. Here the reacted grain surface does not show cracks but is eroded, smoothed and corrugated along particular directions (Fig. 5(c)). Here again the EDX technique shows that the smoothly transformed surfaces have a ternary composition, in contrast with the original surfaces analysed as pure binary.

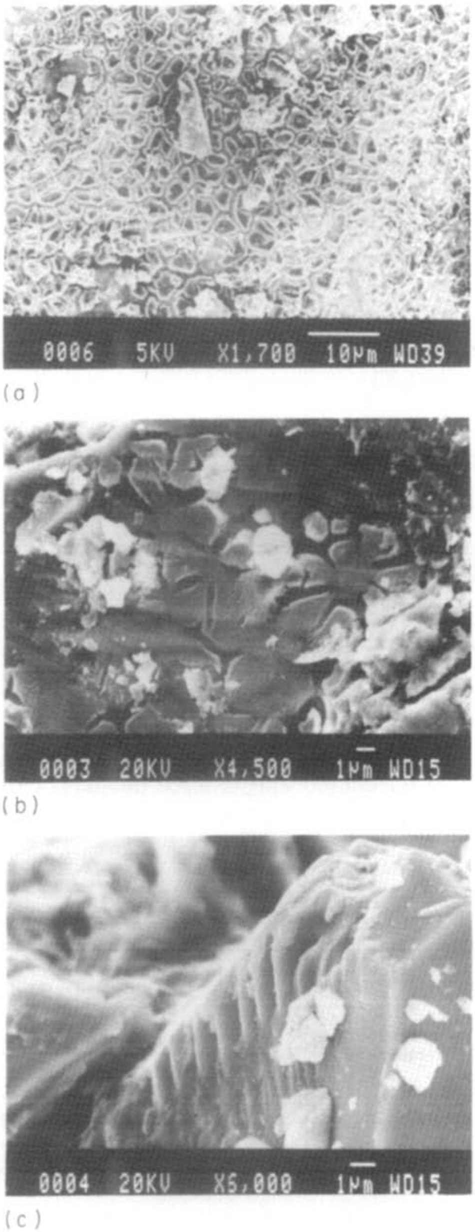


Fig. 5. SEM images of Ho_2Fe_{18} grains reacted with (a, b) anthracene and (c) triazole.

4. Discussion

A new method using organic materials as carbon or/ and nitrogen atom suppliers has been developed and proved to give efficient reactions with R_2Fe_{17} and $R(FeM)_{12}$ alloys, thus transforming them into fully charged ternaries.

The very large increase in Curie temperature (obtained when the alloys are transformed into ternaries) can be strictly correlated with the increase in the mean ⟨Fe–Fe⟩ distance upon C(N) charging, as reported elsewhere [14]. Similarly, the dramatic change in the R crystal electric field parameters is fully achieved when the interstitial sites are fully occupied with respect to the local symmetry (three C or N atoms per formula unit). Therefore the novel method proposed by us leads to the highest quality of interstitial samples, the most interesting fundamental properties and the highest technological performances.

The high temperature cracking of heavy hydrocarbon or hydrocarbonitrogen materials proves to be an efficient method to achieve such a high interstitial content. The rate of the reaction and the resulting products have been checked by using several techniques such as X-ray diffraction, neutron diffraction kinetic experiments, on-line thermomagnetic analysis, SEM and EDX analysis. All these investigations show that the reactions reach completion when using anthracene or triazole as precursor and that the final products are of good quality. The role of hydrogen is not clearly established. However, if the ternary hydrides are not stable at temperatures where the reaction of carbon or nitrogen takes place, hydrogen should play a positive role by activating the surface (chemical reduction) and by facilitating diffusion in the voids (mechanical cracking). The elimination of the final hydrogen overpressure during large scale reactions is relevant for engineering processes, which are made easier if the organic material is selected on the basis of the lowest chemical hazard level.

The characteristic diffusion-controlled rate process appears markedly different for N and C. This could explain why "intermediate" nitride compositions are highly metastable and nitrogen precipitates quickly in heterogeneous regions (the alloy R_2Fe_{17} transforms to $R_2Fe_{17}N_X$ from $x_N \approx 0$ to $x_N \leqslant 3$ through a first-order phase transformation). According to the experimental results, the C diffusion process appears slower, with the larger atomic radius of carbon yielding a larger cell expansion (higher total elastic energy); stabilization of intermediate compositions remains accessible via appropriate thermal treatments.

The magnetic analysis shows that excessively high reaction temperatures lead to the formation of iron precipitates, this disproportionation reaction being a thermally activated process, thus prohibiting reaction temperatures in excess of 500 °C. For example, for the reaction between R_2Fe_{17} and anthracene a good temperature range is between 360 and 450 °C. The upper limit is close to the Curie temperature of the final ternary compound, which facilitates monitoring of the reaction parameters (elapsed time, grain size, pressure, etc.) by means of a thermomagnetic device.

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